Structure determination of aqueous solutions of caesium-halogenides

(booklet of theses of dissertation)

Viktória Mile

supervisor: Dr. László Pusztai

MTA SZFKI

2010

ELTE TTK, Chemistry Doctoral School

Head: Dr. György Inzelt.

Theoretical and Physical Chemistry, Structural Chemistry

Head: Dr. Péter Surján.

Preliminaries

Water is an excellent solvent for ionic and polar solutes and this is why not only studying pure water but also of aqueous solutions is an important field of research. Part of this line of research is the study of electrolyte solutions, as we encounter electrolyte solutions in nearly all areas of our life. My dissertation is focused on the determination of the structure, since for understanding the behaviour of any system it is essential to know the microscopic structure.

A major issue concerning the structure determination of electrolyte solutions is that one cannot achieve an appropriate description of the structure by analysing directly results of available experimental (diffraction) methods. Similarly, description of aqueous solutions based on theories of statistical mechanics is not successful regarding the solution structure. Consequently, the only possible route is to combine the two (experimental and theoretical) approaches in some manner. My PhD dissertation demonstrates one possible realisation of this combination.

The research team of the Neutron Physics Department of RISSPO, HAS has been studying the structure of molecular liquids, including electrolyte solutions (for example solutions of HCl, LiCl, RbBr), systematically for quite some years. My research contributes to this project.

Objectives

The main objective of my doctoral dissertation was to provide an accurate description of the structure of electrolyte solutions; for this purpose, we have attempted to work out a method which is based on experimental (neutron and x-ray diffraction and later, EXAFS) data, but also utilizes to a great extent the results of molecular dynamics (MD) simulations.

Such a method was needed beacuse, at least for systems that have been studied by our group, comparing the structure factors from Molecular Dynamics with experimental structure factors from diffration showed that the MD simulated structure cannot be accepted as physically meaningful in every detail. It is therefore necessery to refine results of MD calculations by means of the available diffraction data. That is, the only possible route is to combine the two (experimental and theoretical/simulation) approaches in some ways. My PhD dissertation demonstrates one possible realisation of this combination.

We have generated models of the liquid structure, consisting thousands of particles, that reproduce diffraction results within the experimental uncertainties and, at the same time, that can be closely connected to computer simulation results.

We tried to introduce and test a method which will, in the future, routinely allow structure

determination of electrolyte solutions by the help of the most basic diffraction measurements and of the outcome of computer simulations.

Naturally, one of the aims was the determination and analyses of the structural parameters (partial radial distribution functions, distributions of the cosines of angles, coordination numbers) of the systems studied.

With the advance of research work we found a new goal connected to potentials used in molecular dynamcis. We have attempted to find the best water models that are worth applying for the computer simulation of simple electrolyte solutions so that the 'pure' MD simulation could be as closely connected to results of diffraction methods as possible.

Methods

Atoms in a liquid do not possess steady positions; instead, correlations between their positions are looked at. That is, the structure can be described by correlation functions.

The problem in the case of multi-component systems is that available diffraction data are insufficient for allowing the calculation of the partial pair correlation functions unambigously.

It was necessary to find a general structural modelling method which can help us to study, by creating large models, the structure of disordered condensed phases beyond the atomic pair correlation function level. It was also important to be able to include information, such as the molecular structure, from non-diffraction sources into the models (which possibly help to reduce the necessary number of diffraction experiments). These requirements can be fulfilled by the *„Reverse Monte Carlo"* (RMC) method [McGreevy, 1988].

This procedure moves atoms in the simulation box via a Monte Carlo algorithm in order to produce (sets of) atomic configurations which are consistent with the measured diffraction data.

In our case the 'non-diffraction' sources were partial radial distribution function from molecular dynamics computer simulations.

The scheme for combining results of diffraction experiments and molecular dynamics computer simulations (using partial rdf's resulting from them) was applied on solutions of rubidium bromide first in [Pusztai, 2008]. As a continuation of this work we have studied systematically, on the one hand, the applicability of the method and, on the other hand and due to some of their advantageous features, the structure of aqueous solutions of caesium-halogenides. Figure 1 shows the main steps of the approach.

For Reverse Monte Carlo (RMC) computer modelling we took into consideration simultane-

ously the results of X-ray and neutron diffraction measurements and of the molecular dynamics calculations. In this way we generated models of the liquid structure, consisting thousands of particles, from which any structural feature of the system can be determined that are calculable from the coordinates of particles.

Results (based on diffraction measurements and MD calculations) that appear in my PhD dissertation have been achieved via Reverse Monte Carlo modelling of molecular liquids. I thank Orsolya Gereben and László Pusztai for providing raw data of MD calculations and diffraction measurements with me, respectively.

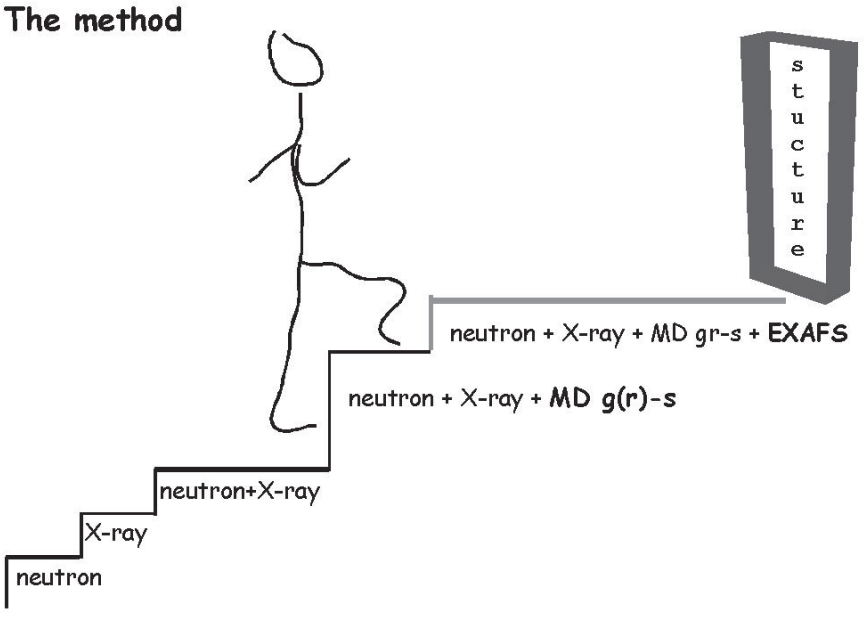

Figure 1: Schematic illustration summarizing the various steps of our approach

New scientific results

1. I have compared structure factors from molecular dynamics (MD) simulations of aqueous solutions of caesium-fluoride, caesium-chloride, caesium-bromide and caesium-iodide with the corresponding functions obtained from x-ray and neutron diffraction experiments. I have found that rigid water models with four sites reproduce experimental data the most closely. Within this category one cannot distinguish between polarizable and non-polarizable models since certain parts of the data are described better by means of polarizable potentials while other parts are described better by means of the non-polarizable ones.

2. Regarding dilute solutions in the case of all water models (rigid, polarizable; rigid non-polarizable; flexible non-polarizable) I have found MD $g_{ij}(r)$-s reflecting the interactions between ions and water consistent with the available experimental results. Fitting $g_{ij}(r)$-s corresponding to water-water interactions was not successful for most of the water models: here, again, models with four sites proved to be better than others. In concentrated solutions inconsistencies also appeared between MD and RMC refined MD $g_{ij}(r)$-s describing cation ? water and the anion ? water correlations.

3. Regarding coordination numbers and their distributions, pure MD calculations and the MD calculations refined by RMC in most cases provided the same results (within the margin of error). For CsF and CsBr solutions I have found larger deviations regarding the number of water molecules around the anion, and in the case of CsF also regarding the number of water molecules around water molecules. These deviations derive from the fact that MD supposes the formation of a more regular (that is, less ?flexible?) H-bond system than that can be connected with the experimental results.

4. With increasing concentration and increasing size of the anion the number of the water molecules present in the hydration sphere of the cation decreases. Numerically, in the hydratation sphere of Cs^+ ions, depending on concentration and–to some extent–the size of the anion, the number of water molecules varies between 8 (dilute solutions) and 5 (concentrated solution).

5. Around the anions, depending on concentration, 7 (dilute solution) - 5 (concentrated solution) water molecules can be found. From the numbers of the hydrogen atoms positioned in the vicinity of anions we can find that the hydratation sphere of the anions is less

diffuse than of the cations. Furthermore, we can declare that most of the water molecules positioned around the anion are connected to the anion exactly by one of their hydrogen atoms (that is, via H-bond).

6. During the study of H-bonds I have found that, in order to be consistent with diffraction data, H-bonds between water molecules have to become much more distorted, as compared to the optimal straight angle, than the ones connecting water molecules and anions.

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List of publication related to the PhD dissertation

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Publications not related to the PhD thesis

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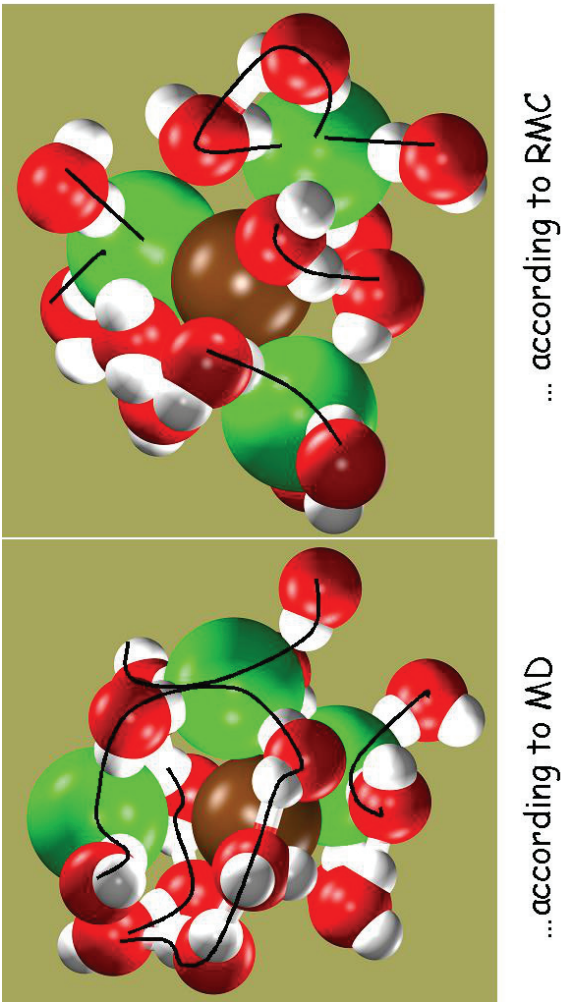

Figure 2: .

Snapshot of the 15 mol% CsCl solution: Cs^+: brown, Cl^-: green, O: red and H: white. We can recognize that in the immediate environment of the Cs^+-ion the hydrogen bonded system of MD (black line) is more regularly arranged as compared to the picture consistent with experiments. Furthermore, we can observe the H-bonds primarily decompose between water molecules while the anion-water relations remain nearly intact.